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(54) Title: **TREATMENT PROCESS FOR CELLULOSIC FIBERS**

## (57) Abstract

Disclosed is a process for treating cellulosic fibers using steam explosion that is effective to result in modified cellulosic fibers that exhibit desired properties such as wet curl values. The steam explosion process is quite efficient and has been found to produce cellulosic fibers that are essentially uniformly treated. Also disclosed is a handsheet prepared from the treated cellulosic fibers for use in disposable absorbent products.

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## TREATMENT PROCESS FOR CELLULOSIC FIBERS

Background of the InventionField of the Invention

The present invention relates to a process for treating cellulosic fibers. The cellulosic fibers prepared from such a process may be used to prepare a handsheet or other structure that may be used in a disposable absorbent product intended for the absorption of fluids such as body fluids. Other possible applications of these fibers include various disposable paper products such as tissue and towel.

Description of the Related Art

Cellulosic fibers are well known and are used in a wide variety of applications. However, natural or generally untreated cellulosic fibers have been found to generally not provide a level of performance that is desired in certain applications such as the absorption or handling of fluids such as body fluids. As such, it is often desirable to increase the liquid absorbent capacity or the resiliency of the cellulosic fibers being used in such applications. Thus, for some applications, it has been recognized that the cellulosic fibers being used should first be structurally modified in order to improve the performance of such modified fibers in a particular application.

One known method for modifying cellulosic fibers is to chemically crosslink the cellulosic fibers. In general, a chemical crosslinking agent is added to either a solution containing cellulosic fibers or to swollen cellulosic fibers. The chemical crosslinking agent is then allowed to form crosslinks either within an individual cellulosic fiber or between separate cellulosic fibers. Such processes inherently result in the use of a separate crosslinking agent thereby increasing the costs of manufacturing the chemically crosslinked cellulosic fibers. Additionally, the use of certain crosslinking agents typically requires specialized handling procedures, further increasing the costs of manufacturing, and potentially limiting the applications for which the chemically crosslinked cellulosic fibers may be used. Another disadvantage concerning the use of chemical crosslinking agents is that they are often based on chemicals such as aldehydes which exhibit certain degrees of toxicity.

A variety of chemical treatments of cellulosic fibers are also known. An example of a well known chemical treatment of cellulosic fibers is a mercerization process wherein

cellulosic fibers are treated with, typically, sodium hydroxide under suitable conditions to convert the cellulose from its native form into a more thermodynamically stable, less crystalline form. Because the mercerized cellulose is less crystalline and more amorphous, the mercerized cellulose is generally more accessible for further treatment with additional reagents.

These and other known processes for chemically treating cellulosic fibers typically disperse the cellulosic fibers in a solvent, such as an aqueous solution. However, it has been generally recognized that in order to ensure proper mixing of the cellulosic fibers and whatever chemicals are being used to treat the cellulosic fibers as well as to ease the bulk transport of the treatment mixture, such known processes must have the cellulosic fibers present in the solvent at a low consistency. Such processes therefore generally result in the use of more of the solvent in which the chemical treatment takes place, or the chemical treatment agent being used, than would ideally be needed, thereby increasing the costs of manufacturing the chemically treated cellulosic fibers. Additionally, the use of sodium hydroxide, or other caustic agents, typically requires specialized handling procedures as well as recycling processes to ensure that such materials are not discharged to the environment.

Another known method for modifying cellulosic fibers is to mechanically treat the cellulosic fibers. One example of such a mechanical treatment process is wherein the cellulosic fibers are subjected to a high shear force which generally results in highly twisted or curled cellulosic fibers. However, such mechanical treatment processes generally require the use of specialized equipment and the use of large amounts of energy, thereby increasing the costs of manufacturing the mechanically treated cellulosic fibers. Besides, without any additional treatment, the fibers modified only by mechanical treatment generally do not preserve their curl in wet conditions because they swell and collapse. Therefore, mechanical modification is generally not quite sufficient for cellulosic fibers which are used for absorbent structures requiring more porosity or capacity.

It is therefore an object of the present invention to provide a process for the preparation of treated cellulosic fibers in which the amount of solvent and chemical treatment agents used in the process is minimized or completely eliminated.

It is also an object of the present invention to provide a process for the preparation of treated cellulosic fibers in which the cellulosic fibers are essentially uniformly treated.

It is also an object of the present invention to provide a process for the preparation of treated cellulosic fibers which will significantly reduce the costs of manufacturing.

It is also an object of the present invention to prepare modified cellulosic fibers that exhibit improved liquid handling properties as compared to untreated cellulosic fibers.

### Summary of the Invention

The present invention concerns an efficient and effective manner for treating cellulosic fibers as well as the treated cellulosic fibers prepared from such a process.

One aspect of the present invention concerns a process for treating cellulosic fibers wherein the cellulosic fibers are treated using steam explosion that is effective to result in modified cellulosic fibers that exhibit desired properties.

One embodiment of such a process for treating cellulosic fibers comprises steam cooking cellulosic fibers in direct contact with saturated steam at a superatmospheric pressure and a temperature within the range of about 130°C to about 250°C, and then subjecting the cellulosic fibers to explosive decompression to give modified cellulosic fibers that exhibit a Curl Index value that is greater than about 0.2.

In another aspect, the present invention concerns the modified cellulosic fibers prepared by the process disclosed herein.

One embodiment of such an aspect of the present invention is modified cellulosic fibers that exhibit a Curl Index value that is greater than about 0.2 that are prepared by a process comprising steam cooking cellulosic fibers in direct contact with saturated steam at a superatmospheric pressure and a temperature within the range of about 130°C to about 250°C, and then subjecting the cellulosic fibers to explosive decompression.

In another aspect, the present invention concerns an absorbent structure comprising modified cellulosic fibers prepared by the process disclosed herein.

One embodiment of such an absorbent structure is a handsheet comprising the modified cellulosic fibers prepared by the process disclosed herein, wherein the handsheet is prepared by a wet-laid process.

### Detailed Description of the Preferred Embodiments

It has been discovered that, by using a steam explosion process for treating cellulosic fibers, and by using appropriate treatment conditions, modified cellulosic fibers exhibiting desired properties may be prepared by an efficient and effective process.

A wide variety of cellulosic fibers can be employed in the process of the present invention. Illustrative cellulosic fibers include, but are not limited to, wood and wood products, such as wood pulp fibers; non-woody paper-making fibers from cotton, from straws and grasses, such as rice and esparto, from canes and reeds, such as bagasse,

from bamboos, from stalks with bast fibers, such as jute, flax, kenaf, cannabis, linen and rami, and from leaf fibers, such as abaca and sisal. It is also possible to use mixtures of one or more cellulosic fibers. Suitably, the cellulosic fiber used is from a wood source. Suitable wood sources include softwood sources such as pines, spruces, and firs, and hardwood sources such as oaks, eucalyptuses, poplars, beeches, and aspens.

As used herein, the term "fiber" or "fibrous" is meant to refer to a particulate material wherein the length to diameter ratio of such particulate material is greater than about 10. Conversely, a "nonfiber" or "nonfibrous" material is meant to refer to a particulate material wherein the length to diameter ratio of such particulate material is about 10 or less.

It is generally desired that the cellulosic fibers used herein be wettable. As used herein, the term "wetable" is meant to refer to a fiber or material which exhibits a water in air contact angle of less than  $90^\circ$ . Suitably, the cellulosic fibers useful in the present invention exhibit a water in air contact angle between about  $10^\circ$  to about  $50^\circ$  and more suitably between about  $20^\circ$  to about  $30^\circ$ . Suitably, a wettable fiber refers to a fiber which exhibits a water in air contact angle of less than  $90^\circ$ , at a temperature between about  $0^\circ\text{C}$  and about  $100^\circ\text{C}$ , and suitably at ambient conditions, such as about  $23^\circ\text{C}$ .

Suitable cellulosic fibers are those which are naturally wettable. However, naturally nonwettable fibers can also be used. It is possible to treat the fiber surfaces by an appropriate method to render them more or less wettable. When surface treated fibers are employed, the surface treatment is desirably nonfugitive; that is, the surface treatment desirably does not wash off the surface of the fiber with the first liquid insult or contact. For the purposes of this application, a surface treatment on a generally nonwettable fiber will be considered to be nonfugitive when a majority of the fibers demonstrate a water in air contact angle of less than  $90^\circ$  for three consecutive contact angle measurements, with drying between each measurement. That is, the same fiber is subjected to three separate contact angle determinations and, if all three of the contact angle determinations indicate a contact angle of water in air of less than  $90^\circ$ , the surface treatment on the fiber will be considered to be nonfugitive. If the surface treatment is fugitive, the surface treatment will tend to wash off of the fiber during the first contact angle measurement, thus exposing the nonwettable surface of the underlying fiber, and will demonstrate subsequent contact angle measurements greater than  $90^\circ$ . Beneficial wettability agents include polyalkylene glycols, such as polyethylene glycols. The wettability agent is used in an amount comprising beneficially less than about 5 weight percent, suitably less than about 3 weight percent, and more suitably less than about

2 weight percent, of the total weight of the fiber, material, or absorbent structure being treated.

In the present invention, it is desired that the cellulosic fibers be used in a form wherein the cellulosic fibers have already been refined into a pulp. As such, the cellulosic fibers will be substantially in the form of individual cellulosic fibers although such individual cellulosic fibers may be in an aggregate form such as a pulp sheet. The current process, then, is in contrast to known steam explosion processes that generally treat cellulosic fibers that are typically in the form of virgin wood chips or the like. Thus, the current process is a post-pulping, cellulosic fiber modifying process as compared to known steam explosion processes that are generally used for high-yield pulp manufacturing or waste-recycle processes.

The cellulosic fibers used in the steam explosion process are desirably low yield cellulosic fibers. As used herein, "low yield" cellulosic fibers are those cellulosic fibers produced by pulping processes beneficially providing a yield of about 85 percent or less, suitably of about 80 percent or less, and more suitably of about 55 percent or less. In contrast, "high yield" cellulosic fibers are those cellulosic fibers produced by pulping processes beneficially providing a yield of about 85 percent or greater. Such pulping processes generally leave the resulting cellulosic fibers with high levels of lignin.

In the process of the present invention, it has been discovered that the use of steam explosion alone can be sufficient to effectively modify cellulosic fibers such that the modified cellulosic fibers exhibit desired properties, particularly desired liquid absorbency properties. In general, it is desired that the cellulosic fibers are cooked in a saturated steam environment that is substantially free of air. The presence of air in the pressurized cooking environment may result in the oxidation of the cellulosic fibers. As such, it is desired that the cellulosic fibers are cooked in a saturated steam environment that beneficially comprises less than about 5 weight percent, suitably less than about 3 weight percent, and more suitably less than about 1 weight percent of air, based on the total weight of the gaseous environment present in the pressurized cooking environment.

The individual cellulosic fibers are steam cooked at a high temperature and at a high pressure. In general, any combination of high pressure, high temperature, and time which is effective in achieving a desired degree of modification, without undesirable damage to the cellulosic fibers, so that the cellulosic fibers exhibit the desired liquid absorbency properties as described herein, is suitable for use in the present invention.

Generally, if the temperature used is too low, there will not be a substantial and/or effective amount of modification of the cellulosic fibers that occurs. Also, generally, if the temperature used is too high, a substantial degradation of the cellulosic fibers may occur which will negatively affect the properties exhibited by the treated cellulosic fibers. As such, as a general rule, the cellulosic fibers will be treated at a temperature within the range beneficially from about 130°C to about 250°C, suitably from about 150°C to about 225°C, more suitably from about 160°C to about 225°C, and most suitably from about 160°C to about 200°C.

Generally, the cellulosic fibers will be subjected to an elevated superatmospheric pressure over a time period within the range of from about 0.1 minute to about 30 minutes, beneficially from about 0.5 minute to about 20 minutes, and suitably from about 1 minute to about 10 minutes. In general, the higher the temperature employed, the shorter the period of time generally necessary to achieve a desired degree of modification of the cellulosic fibers. As such, it may be possible to achieve essentially equivalent amounts of modification for different cellulosic fiber samples by using different combinations of high temperatures and times.

Generally, if the pressure used is too low, there will not be a substantial and/or effective amount of modification of the cellulosic fibers that occurs. Also, generally, if the pressure used is too high, a substantial degradation of the cellulosic fibers may occur which will negatively affect the properties exhibited by the crosslinked cellulosic fibers. As such, as a general rule, the cellulosic fibers will be treated at a pressure that is superatmospheric (i.e. above normal atmospheric pressure), beneficially within the range from about 40 to about 405 pounds per square inch, suitably from about 40 to about 230 pounds per square inch, and more suitably from about 90 to about 230 pounds per square inch.

As used herein, "consistency" is meant to refer to the concentration of the cellulosic fibers present in an aqueous mixture. As such, the consistency will be presented as a weight percent representing the weight amount of the cellulosic fibers present in an aqueous mixture divided by the total weight amount of cellulosic fibers and water present in such mixture, multiplied by 100.

In general, the cellulosic fibers may be used in the process of the present invention in either a dry or a wet state. However, it may be desirable to prepare an aqueous mixture comprising the cellulosic fibers wherein the aqueous mixture is agitated, stirred, or blended to effectively disperse the cellulosic fibers throughout the water. In one embodiment of the present invention, it is desired that the cellulosic fibers be steam



cooked when the cellulosic fibers are in the form of aqueous pulp mixture that beneficially has a consistency of between about 10 to about 100 weight percent, suitably between about 20 to about 80 weight percent, and more suitably between about 25 to about 75 weight percent cellulosic fibers, based on the total weight percent of the aqueous pulp mixture.

The cellulosic fibers are typically mixed with an aqueous solution beneficially comprising at least about 30 weight percent water, suitably about 50 weight percent water, more suitably about 75 weight percent water, and most suitably 100 weight percent water. When another liquid is employed with the water, such other suitable liquids include methanol, ethanol, isopropanol, and acetone. However, the use or presence of such other non-aqueous liquids may impede the formation of an essentially homogeneous mixture such that the cellulosic fibers do not effectively disperse into the aqueous solution and effectively or uniformly mix with the water. Such a mixture should generally be prepared under conditions that are sufficient for the cellulosic fibers and water to be effectively mixed together. Generally, such conditions will include using a temperature that is between about 10°C to about 100°C.

In general, cellulosic fibers are prepared by pulping or other preparation processes in which the cellulosic fibers are present in an aqueous solution. For use in the steam explosion treatment of the present invention, therefore, it may be possible to use an aqueous solution directly from such preparation processes without having to separately recover the cellulosic fibers.

After steam cooking the cellulosic fibers, the pressure is released and the cellulosic fibers are exploded into a release vessel.

The equipment or method used to treat the cellulosic fibers with steam explosion is generally not critical. Suitable equipment and methods for steam explosion may be found, for example, in Canadian Patent No. 1,070,537, dated Jan. 29, 1980; Canadian Patent No. 1,070,646, dated Jan. 29, 1980; Canadian Patent No. 1,119,033, dated Mar. 2, 1982; Canadian Patent No. 1,138,708, dated Jan. 4, 1983; and US Patent 5,262,003, issued November 16, 1993, all of which are incorporated herein in their entirety by reference.

The steam explosion process generally causes the cellulosic fibers to become modified. Without intending to be bound hereby, it is believed that the steam explosion process causes the cellulosic fibers to undergo a curling phenomenon. The steam exploded cellulosic fibers, in addition to being modified, have been discovered to exhibit

improved properties that make such steam exploded cellulosic fibers suitable for use in liquid absorption or liquid handling applications.

Cellulosic fibers suitable for use in the present invention are generally without a substantial amount of curl prior to the steam explosion process. After such steam explosion process, the treated cellulosic fibers will generally exhibit a desired level of stable curl. As such, the process of the present invention generally does not require the use of any additional additives to the cellulosic fibers during the steam explosion process or any post-treatment steps after the steam explosion of the fibers to achieve the desired curls.

In one embodiment of the present invention, the cellulosic fibers will be considered to be effectively treated by the steam explosion process when the cellulosic fibers exhibit an effective Wet Curl value.

The curl of a fiber may be quantified by a curl value which measures the fractional shortening of a fiber due to kink, twists, and/or bends in the fiber. For the purposes of this invention, a fiber's curl value is measured in terms of a two dimensional plane, determined by viewing the fiber in a two dimensional plane. To determine the curl value of a fiber, the projected length of a fiber as the longest dimension of a two dimensional rectangle encompassing the fiber,  $l$ , and the actual length of the fiber,  $L$ , are both measured. An image analysis method may be used to measure  $L$  and  $l$ . A suitable image analysis method is described in U.S. Patent 4,898,642, incorporated herein in its entirety by reference. The curl value of a fiber can then be calculated from the following equation:

$$\text{Curl Value} = (L/l) - 1$$

Depending on the nature of the curl of a cellulosic fiber, such curl may be stable when the cellulosic fiber is dry but may be unstable when the cellulosic fiber is wet. The cellulosic fibers prepared according to the process of the present invention have been found to exhibit a substantially stable fiber curl when wet. This property of the cellulosic fibers may be quantified by a Wet Curl value, as measured according to the test method described herein, which is a length weighted mean curl average of a designated number of fibers, such as about 4000, from a fiber sample. As such, the Wet Curl value is the summation of the individual wet curl values for each fiber multiplied by the fiber's actual length,  $L$ , divided by the summation of the actual lengths of the fibers. It is hereby noted

that the Wet Curl value, as determined herein, is calculated by only using the necessary values for those fibers with a length of greater than about 0.4 millimeter.

As used herein, the cellulosic fibers will be considered to be effectively treated by the steam explosion treatment when the cellulosic fibers exhibit a Wet Curl value that is greater than about 0.2, beneficially between about 0.2 to about 0.4, more beneficially between about 0.2 to about 0.35, suitably between about 0.22 to about 0.33, and suitably between about 0.25 to about 0.33. In contrast, cellulosic fibers that have not been treated generally exhibit a Wet Curl value that is less than about 0.2.

After the cellulosic fibers have been effectively steam exploded, the treated cellulosic fibers are suitable for use in a wide variety of applications. However, depending on the use intended for the treated cellulosic fibers, such treated cellulosic fibers may be washed with water. If any additional processing procedures are planned because of the specific use for which the treated cellulosic fibers are intended, other recovery and post-treatment steps are also well known.

The cellulosic fibers treated according to the process of the present invention are suited for use in disposable absorbent products such as diapers, adult incontinent products, and bed pads; in catamenial devices such as sanitary napkins, and tampons; other absorbent products such as wipes, bibs, wound dressings, and surgical capes or drapes; and tissue-based products such as facial or bathroom tissues, household towels, wipes and related products. Accordingly, in another aspect, the present invention relates to a disposable absorbent product comprising the cellulosic fibers treated according to the process of the present invention.

In one embodiment of the present invention, the treated fibers prepared according to the process of the present invention are formed into a handsheet which might represent a tissue-based product. Such a handsheet may be formed by either a wet-laid or an air-laid process. A wet-laid handsheet may be prepared according to the method disclosed in the Test Methods section herein.

It has been discovered that a wet-laid handsheet prepared from the treated cellulosic fibers prepared according to the process of the present invention may exhibit a density that is lower than a wet-laid handsheet prepared from cellulosic fibers that have not been treated according to the process of the present invention.

It has also been discovered that a wet-laid handsheet prepared from the treated cellulosic fibers prepared according to the process of the present invention may exhibit a liquid wicking time that is faster than a wet-laid handsheet prepared from cellulosic fibers that have not been treated according to the process of the present invention.

It has also been discovered that a wet-laid handsheet prepared from the treated cellulosic fibers prepared according to the process of the present invention may exhibit a liquid wicking flux that is higher than a wet-laid handsheet prepared from cellulosic fibers that have not been treated according to the process of the present invention.

It has also been discovered that a wet-laid handsheet prepared from the treated cellulosic fibers prepared according to the process of the present invention may exhibit an increased bulk and higher absorbent capacity than a wet-laid handsheet prepared from cellulosic fibers that have not been treated according to the process of the present invention.

In one embodiment of the present invention, the treated cellulosic fibers prepared according to the process of the present invention are formed into a fibrous matrix for incorporation into an absorbent structure. A fibrous matrix may take the form of, for example, a batt of comminuted wood pulp fluff, a tissue layer, a hydroentangled pulp sheet, or a mechanically softened pulp sheet. An exemplary absorbent structure is generally described in copending US Patent application, Serial Number 60/008,994, which reference is incorporated herein in its entirety by reference.

A fibrous matrix useful in the present invention may be formed by an air-laying process or a wet-laid process, or by essentially any other process known to those skilled in the art for forming a fibrous matrix.

In one embodiment of the present invention, a disposable absorbent product is provided, which disposable absorbent product comprises a liquid-permeable topsheet, a backsheet attached to the liquid-permeable topsheet, and an absorbent structure positioned between the liquid-permeable topsheet and the backsheet, wherein the absorbent structure comprises treated cellulosic fibers prepared using the process of the present invention.

Exemplary disposable absorbent products are generally described in US-A-4,710,187; US-A-4,762,521; US-A-4,770,656; and US-A-4,798,603; which references are incorporated herein by reference.

Those skilled in the art will recognize materials suitable for use as the topsheet and backsheet. Exemplary of materials suitable for use as the topsheet are liquid-permeable materials, such as spunbonded polypropylene or polyethylene having a basis weight of from about 15 to about 25 grams per square meter. Exemplary of materials suitable for use as the backsheet are liquid-impervious materials, such as polyolefin films, as well as vapor-pervious materials, such as microporous polyolefin films.

Absorbent products and structures according to all aspects of the present invention are generally subjected, during use, to multiple insults of a body liquid. Accordingly, the absorbent products and structures are desirably capable of absorbing multiple insults of body liquids in quantities to which the absorbent products and structures will be exposed during use. The insults are generally separated from one another by a period of time.

One liquid transport property desired of the absorbent structure of the present invention is that the absorbent structure exhibits a Vertical Liquid Flux rate, at a height of about 15 centimeters, suitably of at least about 0.002 grams of liquid per minute per gram per square meter of absorbent structure (gsm) per inch of cross-sectional width of the absorbent structure ( $\text{g}/(\text{min} \cdot \text{gsm} \cdot \text{inch})$ ), more suitably of at least about 0.0025  $\text{g}/(\text{min} \cdot \text{gsm} \cdot \text{inch})$ , most suitably of at least about 0.003  $\text{g}/(\text{min} \cdot \text{gsm} \cdot \text{inch})$ , and up to about 0.1  $\text{g}/(\text{min} \cdot \text{gsm} \cdot \text{inch})$ . As used herein, the Vertical Liquid Flux rate value of an absorbent structure is meant to represent the amount of liquid transported across a boundary a specified vertical distance away from a centralized liquid insult location per minute per normalized quantity of the absorbent structure. The Vertical Liquid Flux rate, at a height of about 15 centimeters, of an absorbent structure may be measured according to the test method described herein.

Another liquid transport property desired of the absorbent structure of the present invention is that the absorbent structure exhibits a Vertical Liquid Flux rate, at a height of about 5 centimeters, suitably of at least about 0.01  $\text{g}/(\text{min} \cdot \text{gsm} \cdot \text{inch})$ , more suitably of at least about 0.015  $\text{g}/(\text{min} \cdot \text{gsm} \cdot \text{inch})$ , most suitably of at least about 0.02  $\text{g}/(\text{min} \cdot \text{gsm} \cdot \text{inch})$ , and up to about 0.5  $\text{g}/(\text{min} \cdot \text{gsm} \cdot \text{inch})$ . The Vertical Liquid Flux rate, at a height of about 5 centimeters, of an absorbent structure may be measured according to the test method described herein.

Another liquid transport property desired of the absorbent structure of the present invention is that the absorbent structure exhibits a Wicking Time value of a liquid to an elevation of 15 centimeters of suitably less than about 3.5 minutes, more suitably less than about 3 minutes, and most suitably less than about 2.5 minutes. As used herein, the Wicking Time value of an absorbent structure is meant to represent the time needed to transport a liquid a specified vertical distance away from a centralized liquid insult location. The Wicking Time value of a liquid to an elevation of 15 centimeters for an absorbent structure may be measured according to the test method described herein.

The absorbent structure of the present invention should have a density such that the absorbent structure exhibits the desired liquid transport properties described herein. The density of an absorbent structure generally determines the porosity, permeability,

and capillary structure of the absorbent structure. If the density of the absorbent structure is too high, the capillaries of the absorbent structure will generally be too small such that the capillaries provide a relatively high capillary tension force but, because of the relatively small capillaries, the permeability of the absorbent structure will be relatively low. If the permeability of the absorbent structure is relatively low, the absorbent structure will generally only transport relatively small amounts of liquid so that the vertical liquid flux rate of the absorbent structure will be relatively low at, for example, each of about 5 centimeters and of about 15 centimeters of height from a source of liquid.

Conversely, if the density of the absorbent structure is too low, the permeability of the absorbent structure will be relatively high. However, the capillaries of the absorbent structure will generally be relatively large such that the capillaries provide a relatively low capillary tension force that results in the absorbent structure being generally unable to quickly transport liquid to relatively high elevations such as about 15 centimeters of height from a source of liquid. Thus, such an absorbent structure may exhibit a relatively high vertical liquid flux rate at a height, for example, of about 5 centimeters of height from a source of liquid but the liquid will move slower and slower, or stop altogether, the higher the front of the wicked liquid. Thus, the vertical liquid flux rate of such an absorbent structure will be relatively low at, for example, about 15 centimeters of height from a source of liquid.

Depending on the stability of the capillary structure of an absorbent structure, the density of the absorbent structure may change as a liquid enters into the capillary structure of the absorbent structure. Generally, the structural stability of the absorbent structure will depend on such factors as the stability, as measured, for example, by shape, curl, stiffness, or resiliency, of the fibers in the absorbent structure as well as the stability of the absorbent structure as a whole. Structural changes of the absorbent structure are even more likely if the absorbent structure is under a stress or pressure as, for example, when the absorbent structure is used in a diaper being worn by a human. Thus, it is desirable that the density of the absorbent structure does not substantially change when the absorbent structure absorbs a liquid or otherwise becomes wet or is under a stress or pressure and/or that the absorbent structure substantially recovers its density after the liquid or stress or pressure is removed from the absorbent structure. The stability of the density of an absorbent structure may be quantified, for example, by the difference in densities exhibited by the absorbent structure when different loads, such as each of loads of about 0.15 pound per square inch and about 0.3 pound per square inch, are applied to the absorbent structure. If the difference in the densities exhibited by

the absorbent structure at the different loads is relatively small, the absorbent structure may be considered to be structurally stable. Another method of characterizing the structure of an absorbent structure is by measuring the void volume of the absorbent structure.

### Test Procedures

#### Wet Curl

The Wet Curl value for fibers was determined by using an instrument which rapidly, accurately, and automatically determines the quality of fibers, the instrument being available from OpTest Equipment Inc., Hawkesbury, Ontario, Canada, under the designation Fiber Quality Analyzer, OpTest Product Code DA93.

A sample of dried cellulosic fibers was obtained. The cellulosic fiber sample was poured into a 600 milliliter plastic sample beaker to be used in the Fiber Quality Analyzer. The fiber sample in the beaker was diluted with tap water until the fiber concentration in the beaker was about 10 to about 25 fibers per second for evaluation by the Fiber Quality Analyzer.

An empty plastic sample beaker was filled with tap water and placed in the Fiber Quality Analyzer test chamber. The <System Check> button of the Fiber Quality Analyzer was then pushed. If the plastic sample beaker filled with tap water was properly placed in the test chamber, the <OK> button of the Fiber Quality Analyzer was then pushed. The Fiber Quality Analyzer then performs a self-test. If a warning was not displayed on the screen after the self-test, the machine was ready to test the fiber sample.

The plastic sample beaker filled with tap water was removed from the test chamber and replaced with the fiber sample beaker. The <Measure> button of the Fiber Quality Analyzer was then pushed. The <New Measurement> button of the Fiber Quality Analyzer was then pushed. An identification of the fiber sample was then typed into the Fiber Quality Analyzer. The <OK> button of the Fiber Quality Analyzer was then pushed. The <Options> button of the Fiber Quality Analyzer was then pushed. The fiber count was set at 4,000. The parameters of scaling of a graph to be printed out may be set automatically or to desired values. The <Previous> button of the Fiber Quality Analyzer was then pushed. The <Start> button of the Fiber Quality Analyzer was then pushed. If the fiber sample beaker was properly placed in the test chamber, the <OK> button of the Fiber Quality Analyzer was then pushed. The Fiber Quality Analyzer then began testing and displayed the fibers passing through the flow cell. The Fiber Quality Analyzer also

displayed the fiber frequency passing through the flow cell, which should be about 10 to about 25 fibers per second. If the fiber frequency is outside of this range, the <Stop> button of the Fiber Quality Analyzer should be pushed and the fiber sample should be diluted or have more fibers added to bring the fiber frequency within the desired range. If the fiber frequency is sufficient, the Fiber Quality Analyzer tests the fiber sample until it has reached a count of 4000 fibers at which time the Fiber Quality Analyzer automatically stops. The <Results> button of the Fiber Quality Analyzer was then pushed. The Fiber Quality Analyzer calculates the Wet Curl value of the fiber sample, which prints out by pushing the <Done> button of the Fiber Quality Analyzer.

#### Preparation of Wet-Laid Handsheet

A 17 inch by 17 inch standard handsheet having a basis weight of about 200 grams per square meter was prepared using a desired fiber sample by using a 16 inch by 16 inch cast bronze wet-laid handsheet former mold, available from Voith Corporation.

A British Disintegrator mixer, available from Testing Machines, Inc., was filled with about 2 liters of distilled water at room temperature (about 23°C) and about 37.3 grams of the fiber sample. The counter on the British Disintegrator was set to zero and the cover was placed on the British Disintegrator. The British Disintegrator was turned on until the counter runs to about 600. Alternatively, the British Disintegrator may be run for about 5 minutes. A bucket was filled with about 8 liters of distilled water. The contents of the British Disintegrator was then also poured into the bucket. All the leftover fiber was also rinsed into the bucket.

The handsheet former, having an about 12 inch deep chamber, was filled with tap water to about 5 inches below the top of the handsheet former chamber. The contents of the bucket were then poured into the handsheet former chamber. A dedicated stirrer was then used to mix the suspension in the handsheet former chamber. The stirrer was moved slowly up and down 6 times to cause small vortexes, but to avoid causing large vortexes, in the square pattern of the handsheet former. The stirrer was then removed and the suspension was drained through the forming screen of the handsheet former. The handsheet former was then opened and two layers of blotting paper were placed on the top of the handsheet. A roller, having the equivalent of about 2.3 pounds of pressure per linear inch, was moved back and forth once on each of the left side, the right side, and the center of the formed handsheet. The blotting paper, with the formed handsheet attached, was then lifted off the forming screen. The blotting paper was then placed on a table such that the formed handsheet faced upwards. An 18 inch by 18 inch, 4 mesh



stainless steel screen was placed on top of the handsheet. The blotting paper, handsheet, and screen were then flipped so that the screen was on the bottom and the blotting paper was on top. The blotting paper was then peeled off of the handsheet, leaving the handsheet on the screen. The edges of the handsheet were fastened to the screen using binder clips. The handsheet was left overnight to air-dry. The handsheet, attached to the screen, was then placed in an oven and dried at about 105°C for about an hour. The handsheet was then removed from the oven and removed from the screen. The handsheet was then ready for evaluation for liquid distribution properties.

#### Bulk and Dry Density of an Absorbent Structure

From a handsheet prepared according to the procedure described herein, a strip of sample handsheet material, having a width of about 2 inches and a length of about 15 inches, was obtained by using a textile saw available, for example from Eastman, Machine Corp., Buffalo, New York. The sample strip was cut at least about 1 inch away from the edge of the handsheet so as to avoid edge effects. The sample strip was marked in about 10 millimeter intervals using water-soluble ink.

To measure the bulk of the sample strip, a bulk meter accurate to at least about 0.01 millimeter, such as a bulk meter available from Mitutoyo Corporation, was used. An about one inch diameter platen was used to measure the bulk, with the platen being parallel to the base of the bulk meter. The bulk of the sample strip was measured in about 50 millimeter intervals along the length of the sample strip and then averaged. The average bulk of the sample strip was then used to calculate the dry density of the sample strip, using the weight and dimensions of the sample strip. The wet density of the sample strip may be similarly determined after the sample strip has evaluated for Liquid Flux values.

#### Wicking Time and Vertical Liquid Flux of an Absorbent Structure

From a handsheet prepared according to the procedure described herein, a strip of sample handsheet material, having a width of about 2 inches and a length of about 15 inches, was obtained by using a textile saw available, for example from Eastman, Machine Corp., Buffalo, New York. The sample strip was cut at least about 1 inch away from the edge of the handsheet so as to avoid edge effects.

The apparatus used for holding a sample material while measuring the Wicking Time and Vertical Liquid Flux values for the sample material consists of male and female halves. The apparatus had a length of about 21 inches and consists of glued Plexiglas.

Small nails are placed in the male bar about one inch apart. The female half has holes drilled to accommodate the nails. A 4 mesh nylon screen was stretched onto the nails. The screen was about one inch shorter than the sample holder at both ends. Reinforcing plates stiffened the bar, preventing the bar from buckling under the tension from the nylon screen. Short, flat, perpendicular bars act as springs to stretch the nylon screen and to keep the sample in place.

The sample strip was placed on the nylon screen, with the bottom end of the sample strip placed lower than the bottom edge of the sample holder such that when the sample strip is positioned on the top of the liquid distribution manifold at the beginning of the experiment, the bottom of the sample strip will just touch the liquid surface. A second 4 mesh nylon screen was stretched and placed on top of the sample strip. Two steel pins were driven through the sample strip at each of 5, 10, 15, and 30 centimeters from the bottom of the sample strip to prevent the movement of the sample strip under the weight of absorbed liquid. The female half of the sample holder was fitted onto the male half. Binder clips were used to keep the assembled holder together.

During the evaluation, the sample strip and the sample holder were contained in a Plexiglas tubular enclosure having an inner diameter of about 7.25 inches and a height of about 24 inches. There is a slit (about 0.25 inch by about 3 inches) in the bottom of the tubular enclosure large enough to allow the tube from the aspirator bottle to the liquid distribution manifold to go through. The tubular enclosure was covered with a flat piece of Plexiglas. Distilled water was sprayed on the walls of the tubular enclosure before the experiment to raise the relative humidity inside the tubular enclosure so as to reduce the evaporation of water from the sample strip during the evaluation. The relative humidity should be maintained at about 90 to about 98 relative humidity during the evaluation. The liquid distribution manifold and the tubular enclosure rest on the top of a Plexiglas plate resting on two lab jacks used for adjustability, stability, and maintaining level.

The aspirator bottle was filled with a 0.9 weight percent sodium chloride aqueous solution. The solution in the aspirator bottle was in equilibrium with the upper edge of the slit in the bottom of the tubular enclosure. The scale was tared. The sample holder was placed on the top of the liquid distribution manifold. A stopwatch was started as soon as the bottom edge of the sample strip touched the surface of the solution. The cover was placed on the top of the tubular enclosure.

The vertical distance of the liquid front traveling up the sample strip and the liquid weight absorbed by the sample strip at various times was recorded. The time versus liquid front height was plotted to determine the Wicking Time at about 5 centimeters and

at about 15 centimeters. The weight of the liquid absorbed by the sample strip from the beginning of the evaluation to about 5 centimeters and to about 15 centimeters height was also determined from the data. The Vertical Liquid Flux value of the sample strip at a particular height was calculated by dividing the grams of liquid absorbed by the sample strip by each of: the basis weight, in grams per square meter, of the sample strip; the time, in minutes, needed by the liquid to reach the particular height; and the width, in inches, of the sample strip.

## EXAMPLES

### Example 1

A cellulosic fiber sample was prepared by dewatering, in a laboratory centrifuge, a never dried southern softwood kraft pulp (available from Kimberly-Clark Corporation under the designation CR54 southern softwood kraft pulp) to form a mixture having a consistency of about 25 weight percent cellulosic fibers. Additional samples having consistencies of about 50 and about 75 weight percent cellulosic fibers were prepared by heating the 25 weight percent mixture at a temperature of about 50°C. Samples of about 200 grams, based on a dry basis of cellulosic fibers, were added to a laboratory steam explosion reactor, available from Stake Tech Ltd., Canada. The reactor had a capacity of 2 liters. After closing the top valve, steam at a specific temperature was injected into the reactor. The pulp fibers were directly contacted with the steam for a period of time. The cellulosic fibers were then explosively decompressed and discharged to a container by opening the bottom valve. The steam-exploded fibers were collected for evaluation.

The results of these evaluations are summarized in Table 1, which lists the consistency of the cellulose fiber pulps used; the temperatures used; the amount of time the cellulosic fiber sample was retained in the pressure vessel; and the Curl Index values for the samples. The cellulosic fiber samples were then formed into handsheets according to procedure described herein and the formed handsheets were evaluated for density and Vertical Liquid Flux values.

Those skilled in the art will recognize that the present invention is capable of many modifications and variations without departing from the scope thereof. Accordingly, the detailed description and examples set forth above are meant to be illustrative only and are not intended to limit, in any manner, the scope of the invention as set forth in the appended claims.

Table 1

Temp rature (°C)	Consistency (%)	Time (minutes)	Wet Curl Index	Density (g/cc)	Vertical Liquid Flux (g/min/gsm/inch)
*None	--	--	0.15	0.203	0.0012
160	25	2	0.236	0.219	0.0015
160	25	4	0.224	0.211	0.0019
160	25	6	0.251	0.211	0.0018
160	50	2	0.250	0.200	0.0022
160	50	4	0.242	0.199	0.0021
160	50	6	0.238	0.200	0.0021
160	75	2	0.250	0.181	0.0024
160	75	4	0.267	0.189	0.0024
160	75	6	0.256	0.184	0.0022
180	25	2	0.265	0.214	0.0019
180	25	4	0.236	0.214	0.0020
180	25	6	0.269	0.199	0.0024
180	50	2	0.270	0.192	0.0024
180	50	4	0.298	0.192	0.0023
180	50	6	0.298	0.195	0.0026
180	75	2	0.273	0.182	0.0026
180	75	4	0.294	0.181	0.0026
180	75	6	0.295	0.180	0.0027
200	25	2	0.231	0.206	0.0020
200	25	4	0.29	0.206	0.0021
200	25	6	0.282	0.202	0.0020
200	50	2	0.294	0.193	0.0021
200	50	4	0.298	0.199	0.0020
200	50	6	0.298	0.199	0.0021
200	75	2	0.315	0.188	0.0026
200	75	4	0.31	0.182	0.0026
200	75	6	0.324	0.174	0.0025

\*Not an example of the present invention

What is claimed is:

1. A process for the treatment of cellulosic fibers, the process comprising steam cooking cellulosic fibers in direct contact with saturated steam at a superatmospheric pressure and a temperature within the range of about 130°C to about 250°C, and then subjecting the individualized cellulosic fibers to explosive decompression to give modified cellulosic fibers that exhibit a Wet Curl value that is greater than about 0.2.
2. The process of Claim 1 wherein the cellulosic fibers are from a wood source.
3. The process of Claim 1 wherein the cellulosic fibers are low yield cellulosic fibers.
4. The process of Claim 1 wherein the cellulosic fibers are in the form of individual cellulosic fibers.
5. The process of Claim 1 wherein the cellulosic fibers are treated at a temperature that is between about 150°C to about 225°C.
6. The process of Claim 5 wherein the cellulosic fibers are treated at a temperature that is between about 160°C to about 225°C.
7. The process of Claim 6 wherein the cellulosic fibers are treated at a temperature that is between about 160°C to about 200°C.
8. The process of Claim 1 wherein the cellulosic fibers are treated for an amount of time that is between about 0.1 minute to about 30 minutes.
9. The process of Claim 1 wherein the cellulosic fibers are treated in the form of a pulp having a consistency between about 20 to about 80 weight percent of the cellulosic fibers, based on total weight of the pulp.
10. The process of Claim 1 wherein the cellulosic fibers are treated at a pressure of between about 40 to about 405 pounds per square inch.
11. The process of Claim 1 wherein the saturated steam is substantially free of air.
12. The process of Claim 1 wherein the cellulosic fibers exhibit a Wet Curl value that is between about 0.2 to about 0.4.

13. The process of Claim 12 wherein the cellulosic fibers exhibit a Wet Curl value that is between about 0.22 to about 0.33.
14. A modified cellulosic fiber that is prepared by a process comprising steam cooking cellulosic fibers in direct contact with saturated steam at a superatmospheric pressure and a temperature within the range of about 130°C to about 250°C, and then subjecting the cellulosic fibers to explosive decompression to give modified cellulosic fibers that exhibit a Curl Index value that is greater than about 0.2.
15. The modified cellulosic fiber of Claim 14 wherein the cellulosic fiber is from a wood source.
16. The modified cellulosic fiber of Claim 14 wherein the cellulosic fibers are low yield cellulosic fibers.
17. The modified cellulosic fiber of Claim 14 wherein the cellulosic fibers are in the form of individual cellulosic fibers.
18. The modified cellulosic fiber of Claim 14 wherein the cellulosic fibers are treated at a temperature that is between about 150°C to about 225°C.
19. The modified cellulosic fiber of Claim 18 wherein the cellulosic fibers are treated at a temperature that is between about 160°C to about 225°C.
20. The modified cellulosic fiber of Claim 19 wherein the cellulosic fibers are treated at a temperature that is between about 160°C to about 200°C.
21. The modified cellulosic fiber of Claim 14 wherein the cellulosic fibers are treated for an amount of time that is between about 0.1 minute to about 30 minutes.
22. The modified cellulosic fiber of Claim 14 wherein the cellulosic fibers are treated in the form of a pulp having a consistency between about 20 to about 80 weight percent of the cellulosic fibers, based on total weight of the pulp.
23. The modified cellulosic fiber of Claim 14 wherein the cellulosic fibers are treated at a pressure of between about 40 to about 405 pounds per square inch.
24. The modified cellulosic fiber of Claim 14 wherein the modified cellulosic fiber exhibits a Wet Curl value that is between about 0.2 to about 0.4.

25. The modified cellulosic fiber of Claim 26 wherein the modified cellulosic fiber exhibits a W t Curl value that is between about 0.22 to about 0.33.
26. An absorbent structure comprising wettable cellulosic fibers, wherein the absorbent structure exhibits a Vertical Liquid Flux rate value at a height of about 15 centimeters of at least about 0.002 grams of liquid per minute per gram per square meter of absorbent structure per inch of cross-sectional width of the absorbent structure, wherein the wettable cellulosic fibers are prepared according to the process of Claim 1.
27. An absorbent structure comprising wettable cellulosic fibers, wherein the absorbent structure exhibits a Vertical Liquid Flux rate value at a height of about 15 centimeters of at least about 0.002 grams of liquid per minute per gram per square meter of absorbent structure per inch of cross-sectional width of the absorbent structure.

## INTERNATIONAL SEARCH REPORT

Int. Application No

PCT/US 97/23216

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 D21C9/00 A61F13/15

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 97 23184 A (KIMBERLY CLARK CO) 3 July 1997	27
Y	see abstract see page 2, line 21 - line 23	1-8, 11, 12, 14-21, 23, 24, 26
Y	see page 4, line 15 - page 5, line 32 see page 6, line 21 - line 34 EP 0 153 182 A (JUJO PULP) 28 August 1985  see examples	1-8, 11, 12, 14-21, 23, 24, 26

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR 2 592 400 A (INST TEXTILE DE FRANCE) 3 July 1987 see page 5, line 3 - line 23; claims 9-11 -----	1,4-11, 14,17-23
A	DATABASE WPI Section Ch, Week 8747 Derwent Publications Ltd., London, GB; Class F09, AN 87-331306 XP002064419 & JP 62 236 802 A (ASAHI CHEM IND CO LTD) see abstract -----	1,14

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9723184 A	03-07-1997	AU 1337597 A	17-07-1997
EP 0153182 A	28-08-1985	JP 1603235 C	29-03-1991
		JP 2012494 B	20-03-1990
		JP 60173001 A	06-09-1985
FR 2592400 A	03-07-1987	BR 8607038 A	22-12-1987
		CN 1015652 B	26-02-1992
		EP 0253828 A	27-01-1988
		WO 8704194 A	16-07-1987
		JP 63502520 T	22-09-1988
		KR 9405920 B	24-06-1994